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Ion-Mediated Hydrogen-Bond Rearrangement Through Tunneling in the Iodide–Dihydrate Complex

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A microscopic picture of hydrogen-bond structure and dynamics in ion hydration shells remains elusive. Small ion–dihydrate molecular complexes represent ideal systems to investigate the interplay and competition between ion–water and water–water interactions. Here, state-of-the-art quantum dynamics simulations provide evidence for tunneling in hydrogen-bond rearrangements in the iodide–dihydrate complex and show that it can be controlled through isotopic substitutions. We find that the iodide ion weakens the neighboring water–water hydrogen bond, leading to faster water reorientation than in the analogous water trimer. These faster dynamics, which are apparently at odds with the slowdown observed in the first hydration shell of iodide in solution, can be traced back to the presence of a free OH bond in the iodide–dihydrate complex, which effectively triggers the overall structural rearrangements within it. Besides providing indirect support for co-operative hydrogen-

bond dynamics in iodide solutions, the analysis presented here suggests that iodide ions may accelerate hydrogen-bond rearrangements at aqueous interfaces, where neighbouring water molecules can be undercoordinated.

Determining the driving forces that govern ion hydration is key to the molecular-level understanding of a broad range of chemical transformations in aqueous environments. For example, ions play important roles in acid-base chemistry and catalytic processes,^{1,2} in the stabilization of biomolecules, as well as in mediating protein-protein interactions and intracellular signal transduction.³⁻⁵ In the atmosphere, ionic clusters carry electric currents and are involved in the formation and evolution of aerosol particles.^{6,7} In materials science, ionic solutions are central to many devices, including electrolytic cells, capacitors, and batteries.⁸

Because of long-range Coulomb interactions, ions do not exist as isolated species under equilibrium in the gas phase but form neutral ionic aggregates (e.g., ionic salts). Completely different behavior is observed when ions are dissolved in water. In this case, ion-ion interactions are mediated by the presence of water molecules that allow ions to exist as individual solvated species, up to saturation. Ion stabilization in aqueous solutions results from the interplay between ion-water interactions, which primarily depend on the nature of the ion, and entropic contributions, which are associated with solvent reorganization around the charged species. Although the water hydrogen-bond (H-bond) network is expected to adapt to the presence of ions, the extent to which its structural, thermodynamic, and dynamical properties change, remains an open question.⁹

Halide ions represent a prototypical class of ionic systems, exhibiting large variations in

size, charge density, and polarizability. General correlations have been derived between the chemical nature of these ions and the properties of the surrounding H-bond network in solution, with smaller fluoride ions, on one hand, establishing stronger H-bonds with water, while larger and more polarizable iodide ions, on the other hand, inducing relatively larger structural rearrangements on the surrounding H-bond network, at least locally. Ultrafast vibrational spectroscopy experiments indicate that the dynamics of water in the first solvation shells of halide ions is significantly slowed down compared to that observed in pure water.¹⁰ Ion specific effects have been found at the air/water interface, suggesting that larger and more polarizable halide ions, such as iodide, may exhibit relatively higher propensity for the interface than smaller halides and cations.^{6,11}

Given recent advances in high-resolution vibrational spectroscopy as well as progress in the development of accurate quantum dynamics methods, small halide–water clusters represent ideal systems for characterizing the interplay between ion–water and water–water interactions, energetic and entropic contributions, and nuclear quantum effects in H-bond rearrangements around individual halide ions.^{12–18} Measurements of vibrational predissociation spectra combined with successive isotopic substitutions have allowed for precisely probing possible H-bonding environments and monitoring their evolution as a function of temperature.^{19,20} In particular, vibrational spectra of the iodide–dihydrate complex, $\text{I}^-(\text{H}_2\text{O})_2$,^{19,20} measured at low temperature in the water OH bond stretching region exhibit a well-defined pattern consisting of four distinct peaks at 3344 cm^{-1} , 3516 cm^{-1} , 3619 cm^{-1} , and 3684 cm^{-1} . These peaks can be assigned to specific H-bonding environments within the minimum energy structure of $\text{I}^-(\text{H}_2\text{O})_2$, corresponding to a “closed” configuration with an intact water–water H-bond (Figure 1). As the temperature increases above 50 K,

a new, broad peak starts emerging at 3440 cm^{-1} which is accompanied by the simultaneous disappearance of the initial pattern observed at low temperature, indicating that the complex undergoes significant temperature-dependent H-bond rearrangements.

In this study, we combine state-of-the-art quantum simulations with many-body representations of the underlying molecular interactions to provide a microscopic characterization of the temperature-dependent H-bond dynamics in $\text{I}^-(\text{H}_2\text{O})_2$. Our analysis provides unambiguous evidence for H-bond rearrangements via tunneling mediated by the presence of the iodide ion. Through selective isotopic substitutions, we further demonstrate that tunneling is still observed, although to a lesser extent, in $\text{I}^-(\text{D}_2\text{O})_2$, while it is suppressed in the asymmetric $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue, in which the hydrogen atom remains locked-in in the free position at low temperature. As the water–water H-bond starts breaking at temperatures above $\sim 75\text{ K}$, the complex transitions from the “closed” to an “open” configuration, corresponding to a dynamic configuration with two dangling water molecules H-bonded to the iodide ion but not to each other, which becomes the most stable structure of the complex above 150 K (see Section S2 of the Supplementary Information).

Results

Tunneling pathways and ground-state H-bond rearrangements. As shown in Figure 1, the minimum energy structure of the iodide–dihydrate complex, corresponding to the “closed” configuration, is characterized by a double-donor (DD) water molecule that donates single H-bonds

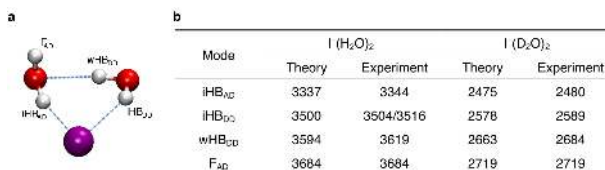


Figure 1: **Ground-state geometry and OH vibrational frequencies of the iodide–dihydrate complex.**

a, Global minimum energy (“closed”) configuration of the iodide–dihydrate complex.

The iodide ion (I^-) is shown in purple, while the oxygen (O) and hydrogen (H) atoms of the water molecules are shown in red and white, respectively. The H atoms of the double-donor (DD) water molecule are labeled as iHB_{DD} and wHB_{DD} to indicate the two H-bonds to the iodide ion and AD water molecule, respectively. The H atoms of the AD water molecule are labeled as iHB_{AD} and F_{AD} to indicate the H-bond to the iodide ion and the free OH bond, respectively.

b, Theoretical and experimental²⁰ OH and OD stretching frequencies (in cm^{-1}) of $I^-(\text{H}_2\text{O})_2$ and $I^-(\text{D}_2\text{O})_2$ complexes in the corresponding global minimum energy configurations.

to both the iodide ion, and a second water molecule that acts as a single-donor/single-acceptor (DA), donating one H-bond to the iodide ion and having one free OH bond. Since the four OH bonds in $I^-(\text{H}_2\text{O})_2$ experience different H-bonding environments, they are associated with distinct stretching frequencies, spanning a range of $\sim 400 \text{ cm}^{-1}$. For both $I^-(\text{H}_2\text{O})_2$ and $I^-(\text{D}_2\text{O})_2$, the anharmonic frequencies calculated by combining the local-mode^{21,22} and local-monomer²³ methods with the iodide-water MB-nrg many-body potential energy function (PEF) of Ref. 24 are always within 25 cm^{-1} of the corresponding experimental values, providing support for the accuracy of the theoretical approach employed in this study.²⁵

It has been established that tunneling pathways leading to H-bond rearrangements, and tun-

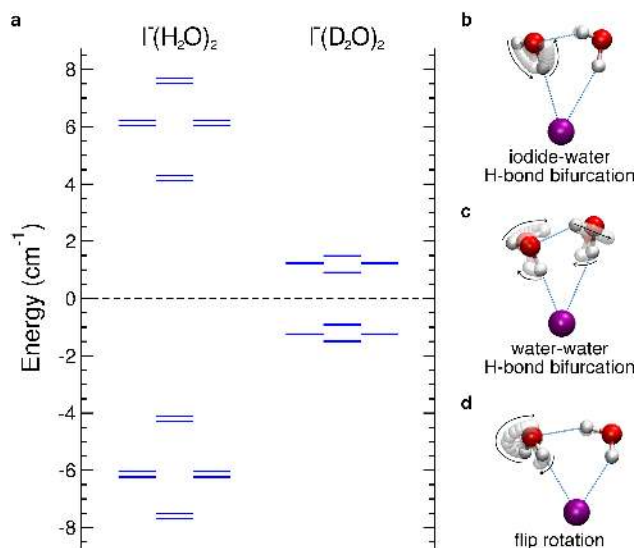


Figure 2: **Tunneling pathways in the iodide–dihydrate complex.** **a**, Ground-state tunneling splitting patterns in the I⁻(H₂O)₂ (*left*) and I⁻(D₂O)₂ (*right*) isotopologues of the iodide–dihydrate complex which result from the iodide–water (**b**) and water–water (**c**) H-bond bifurcations, and flip rotation (**d**) tunneling pathways shown in the schematics. The doublets in the splitting patterns of I⁻(D₂O)₂ are not resolved on this energy scale.

neling splittings of otherwise degenerate energy levels, exist in halide–water dimers^{15,17,18} as well as in the water trimer, which, in its minimum energy configuration, exhibits a cyclic structure analogous to that of the iodide–dihydrate complex.^{26–29} To determine possible ground-state (0 K) tunneling pathways and associated tunneling splittings, in I⁻(H₂O)₂ and its isotopologue, I⁻(D₂O)₂, ring-polymer instanton (RPI) calculations^{29,30} are performed (see Section S1 of the Supplementary Information for specific details). Three feasible tunneling pathways, namely, iodide–water H-bond bifurcation, water–water H-bond bifurcation, and flip rotation are identified as shown in Figure 2a. Each of the first two pathways involves the breaking and forming of a single H-bond, while the third

pathway corresponds to the out-of-plane rotation of the free OH bond of the DA water molecule. The associated energy splitting patterns calculated by diagonalizing the corresponding tunneling matrices²⁹ are shown in Figure 2b and 2c. Within the RPI formalism, the dimensions of the tunneling matrices represent the number of identical versions of each molecular complex, 16 in the case of the iodide–dihydrate complex, which are generated through permutations of the hydrogen (or deuterium) atoms and the inversion operation.^{29,30} Each off-diagonal matrix element corresponds to the tunneling associated with a distinct pathway connecting two different versions of the same complex.²⁹ The individual tunneling matrix elements associated with the three tunneling pathways are given in Table 1. The full 16x16 tunneling matrix used in the calculations of the tunneling splitting patterns and the resulting tunneling timescales is provided in Section S4 of the Supplementary Information. As expected, given the heavier mass of deuterium, the RPI calculations predict smaller tunneling splittings for $I^-(D_2O)_2$ than $I^-(H_2O)_2$.

The RPI results provide unambiguous evidence for the existence of well-defined tunneling pathways. However, current experimental vibrational spectra for ionic clusters are not able to resolve such fine detail. Instead, determining the associated timescales is critical to guiding comparisons between theory and experiment. The tunneling dynamics within the different isotopologues of the iodide–dihydrate complex, $I^-(H_2O)_2$, $I^-(D_2O)_2$, and $I^-(HOD)(D_2O)$, can be determined by monitoring the time evolution of the corresponding H-bond arrangements through propagation of the time-dependent Schrödinger equation under the action of the tunneling Hamiltonian (see Section S4 of the Supplementary Information). Here, we assume that at low enough temperature, only the lowest tunnelling-vibrational states will be occupied. Figures 3a and 3b show, respectively,

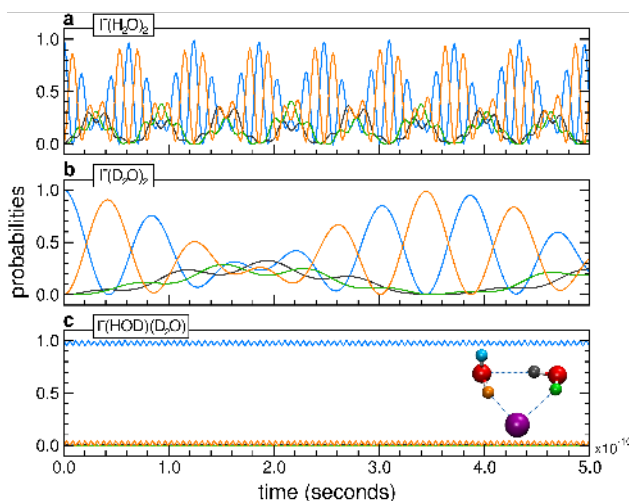


Figure 3: **Tunneling timescales in the isotopologues of the iodide–dihydrate complex.** **a**, Time-evolution of the probabilities for each of the four OH positions in the $\text{I}^-(\text{H}_2\text{O})_2$ isotopologue (shown with the corresponding colors in the inset in panel **c**) to be occupied by the H atom located in the free OH position at time $t = 0$. **b**, Same analysis as in **a** performed for the OD positions in the $\text{I}^-(\text{D}_2\text{O})_2$ isotopologue. **c**, Same analysis as in **a** performed for the OH positions in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue.

the probabilities for a hydrogen atom of $\text{I}^-(\text{H}_2\text{O})_2$ and a deuterium atom of $\text{I}^-(\text{D}_2\text{O})_2$, initially located in the free position ($t = 0$, blue trace), to be found in any of the four different positions, represented by the four different colors (see schematic in Figure 3), at a later time t . Also shown in Figure 3c are the corresponding probabilities for the hydrogen atom of HOD in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$. As expected from the tunneling splitting values, $\text{I}^-(\text{H}_2\text{O})_2$ displays faster tunneling dynamics compared to $\text{I}^-(\text{D}_2\text{O})_2$. On the other hand, in the ground state of $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$, the hydrogen atom is predicted to remain effectively locked-in in the free position. Here, we assume that the coupling between wells is the average of the $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ clusters, but that the zero-point energy

of each well is different. It is thus the asymmetry within the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ complex which leads to the destruction of the quantum coherence.

Direct insights into the effects of iodide on the water–water H-bond rearrangement are gained from the comparison reported in Table 1 between the tunneling matrix elements calculated for both $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$, and the corresponding values for the water dimer and trimer.²⁹ Although both water–water H-bond bifurcation and flip rotation follow pathways similar to those found in pure water complexes, the tunneling probabilities, which, for degenerate rearrangements, are inversely proportional to the associated tunneling splittings (see Section S4 of the Supplementary Information), are significantly different. In particular, the water–water H-bond bifurcation dynamics in the iodide–dihydrate complex is orders of magnitude faster than in the water trimer. The presence of the iodide ion drastically weakens the neighboring water–water H-bond, resulting in an energy barrier for the water–water H-bond bifurcation in the iodide–dihydrate complex of 0.52 kcal/mol, which is more than a factor of four lower than that in the water trimer (~ 2.34 kcal/mol). Importantly, the flip rotation in the pure water complexes is faster than all water-water H-bond bifurcations, since it does not require breaking any H-bond. However, the same trend is not followed in the iodide–dihydrate complex for which the flip rotation is particularly slow. This slower dynamics is explained by considering that the energy barrier for the flip rotation (1.11 kcal/mol) in the iodide–dihydrate complex is more than two times higher than those associated with the iodide–water (0.47 kcal/mol) and water–water (0.52 kcal/mol) H-bond bifurcations, and more than four times higher than those associated with flip rotation in the water trimer (0.24 kcal/mol).²⁹ The high energy barrier in the iodide–dihydrate complex could be attributed to the large positive change in

the electrostatics interactions in the planar transition state relative to the minimum energy configuration (see Section S4 of the Supplementary Information).

Since minimal rearrangement of the oxygen atoms is required for the iodide–water H-bond bifurcation, the associated pathway is characterized by a potential energy barrier that is lower by ~ 0.06 kcal/mol and narrower by $\sim 24^\circ$, in full width at half maximum, than that found along the water–water H-bond bifurcation (see Figure 4). As a consequence, the iodide–water H-bond bifurcation is faster than the water–water H-bond bifurcation, resulting in a larger tunneling splitting. The difference between the H-O-I angles (denoted as α), corresponding to the free OH bond, and the H-bonded-to-iodide OH bond within the same water molecule is used in Figure 4 as a collective variable to describe the iodide–water H-bond bifurcation pathway. The difference between the H-O-I-O' dihedrals (denoted as δ), corresponding to the free OH bond, and the H-bonded-to-water OH bond is used as a collective variable for the water–water H-bond bifurcation pathway. It should be noted that, although the shape of the two barriers would be different if only one angle (dihedral) would be used instead of the difference between two angles (dihedrals), the relative differences between the two barriers would be independent of the specific choice of the collective variable.

Temperature-dependence and H-bond dynamics. Previous studies determined that the water–water H-bond in the iodide–dihydrate complex starts breaking at ~ 100 K, which leads to an open configuration with two dangling water molecules H-bonded to the iodide ion. To monitor the equilibrium between closed and open configurations and characterize the effects of tunneling on the H-bond dynamics as a function of temperature, path-integral molecular dynamics (PIMD) simula-

tions are carried out for $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ between 10 K and 200 K. In agreement with the analysis of vibrational predissociation spectra,¹⁹ PIMD simulations predict that both complexes exist predominantly in closed configurations below 100 K (see Section S2 of the Supplementary Information).

Additional insights into the role played by tunneling in H-bond rearrangements within $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ at finite temperature can be gained from the analysis of one-dimensional quantum free energies along the two collective variables describing iodide–water and water–water H-bond bifurcations calculated from the PIMD trajectories which are shown in Figure 4. For comparison,

Table 1: Comparisons with analogous water complexes. Tunneling matrix elements, $-\hbar$, (in cm^{-1}) for the iodide–water and water–water H-bond bifurcations, and flip rotation pathways calculated for the water dimer and trimer (Ref. 29), and $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ isotopologues of the iodide–dihydrate complex (this work). It should be noted that the flip rotation in the water dimer follows a slightly different mechanism from that observed in the water trimer and iodide–dihydrate complex, which, however, still does not involve the breaking of any hydrogen bonds as in the other two complexes.

	$(\text{H}_2\text{O})_2$	$(\text{H}_2\text{O})_3$	$\text{I}^-(\text{H}_2\text{O})_2$	$(\text{D}_2\text{O})_2$	$(\text{D}_2\text{O})_3$	$\text{I}^-(\text{D}_2\text{O})_2$
iodide–water bifurcation	-	-	5.9	-	-	1.2
water–water bifurcation	0.035	~ 0.01	1.7	2.7E-4	3.0E-5	0.29
flip rotation	5.5	50	0.09	0.6	18	3.4E-3

also shown are the associated minimum energy paths on the underlying Born-Oppenheimer potential energy surface. Below 50 K, both quantum free energy barriers for the two H-bond bifurcations are significantly lower than the corresponding Born-Oppenheimer potential energy barriers. This implies that the OH and OD bonds in $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$, respectively, undergo frequent interconversions between the four equivalent positions through the same large amplitude rotational tunneling motions identified by the RPI calculations. This complete “scrambling” of H-bonds emphasizes the purely quantum nature of both complexes at low temperature.

The interplay among ion–water and water–water interactions, entropic contributions, and nuclear quantum effects in the iodide–dihydrate complex can be further characterized by investigating temperature-dependent H-bond rearrangements in the mixed isotopologue, $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$. Isotopic substitution has been shown to be a powerful tool for determining H-bond rearrangements in water through vibrational spectroscopy, often enabling unambiguous spectral assignments which would be otherwise difficult to make due to strong inter-mode couplings.²⁰ Since the four distinct positions that the hydrogen atom can occupy within $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ are associated with different zero-point energies and entropic contributions, the total free energy of the complex in its closed configuration thus depends on the specific location of the hydrogen atom.

As shown in Figure 3c, the RPI calculations indicate that tunneling in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ is completely suppressed at low temperatures, with the hydrogen atom remaining locked-in in the free position. To monitor the evolution of the H-bond dynamics as a function of temperature, PIMD simulations are carried out to calculate two-dimensional quantum free-energy surfaces, using the

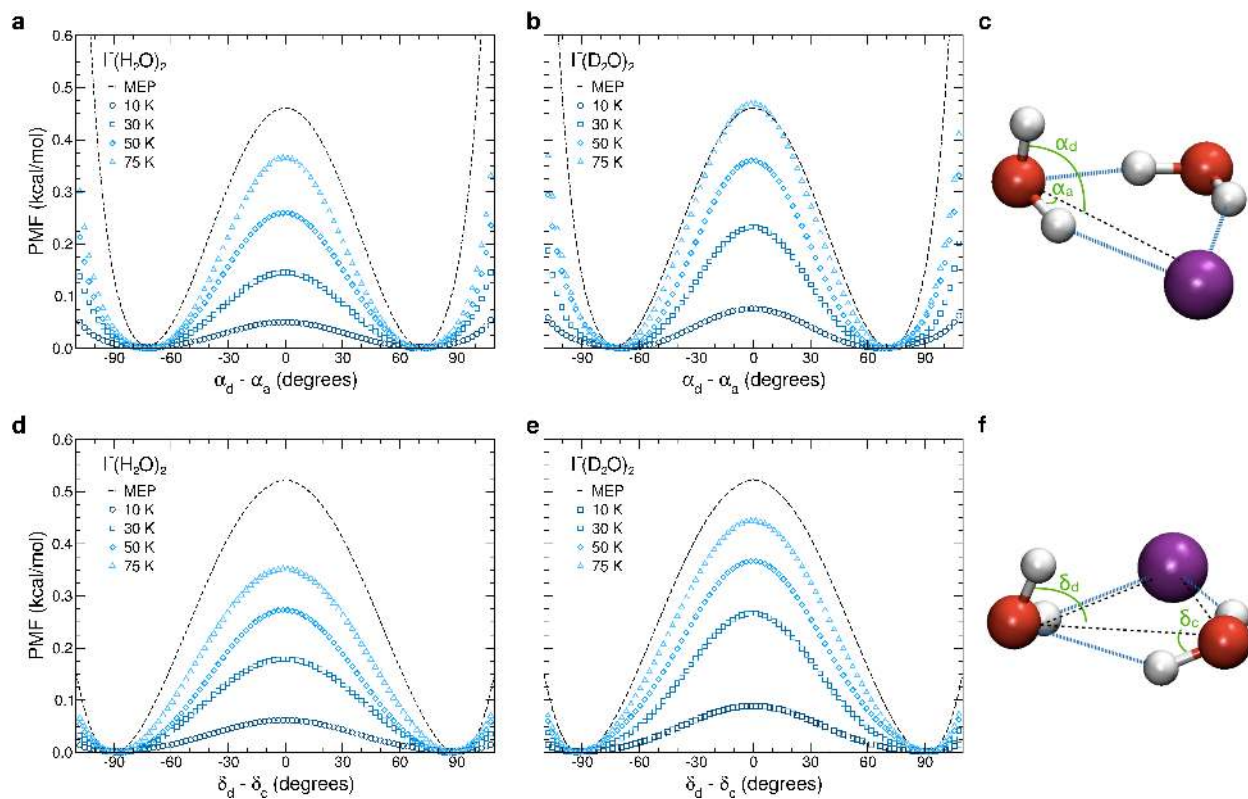


Figure 4: Temperature-dependent free energies along the tunneling pathways. **a** and **b**, One-dimensional quantum potential of mean forces (PMFs) along the iodide–water H-bond bifurcation pathway (defined by the collective variable $\alpha_d - \alpha_a$) of the $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ isotopologues, respectively, calculated from the corresponding PIMD well-tempered metadynamics simulations. **c**, Schematic representation of α_a and α_d in the iodide–dihydrate complex. **d** and **e**, One-dimensional quantum potential of mean forces (PMFs) along the water–water H-bond bifurcation pathway (defined by the collective variable $\delta_d - \delta_c$) of the $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ isotopologues, respectively, calculated from the corresponding PIMD well-tempered metadynamics simulations. **f**, Schematic representation of δ_c and δ_d in the iodide–dihydrate complex.

well-tempered metadynamics biasing approach,³¹ along the H-O-I angle and H-O-I-O' dihedral angle which are employed as collective variables describing the iodide–water and water–water H-bond bifurcation motions, respectively (top panels of Figure 5). Also shown in the bottom panels of Figure 5 are the one-dimensional quantum free-energy curves associated with the two H-bond bifurcations along with the corresponding Born-Oppenheimer minimum potential energy paths analogous to those shown in Figure 4.

At 10 K, the configuration with the hydrogen atom in the free position still corresponds to the most stable structure of $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$, lying approximately 0.1 kcal/mol below the other three configurations with the hydrogen atom in H-bonded positions. It should be noted that configuration 4 (see Figure 5), with the hydrogen atom belonging to the DD water molecule and H-bonded to the iodide ion, is not part of any direct bifurcation pathway and can only be reached through a second-order dynamical process involving the iodide-water H-bond bifurcation followed by the water-water H-bond bifurcation pathways. Besides breaking the symmetry of the 1D quantum free-energy profiles along both bifurcation pathways, the presence of the hydrogen atom in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ also modifies the associated quantum free-energy barriers that become approximately three times higher than in the pure $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ complexes, but still appreciably lower than the corresponding barriers on the underlying Born-Oppenheimer potential energy surface. This suggests that tunneling may possibly occur in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ at finite temperature although to a lesser extent than in $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$. The average relative populations of the four different positions, however, will depend on the availability of accessible vibrational states at a particular temperature, governed by the Boltzmann distribution function. As shown in Figure 5,

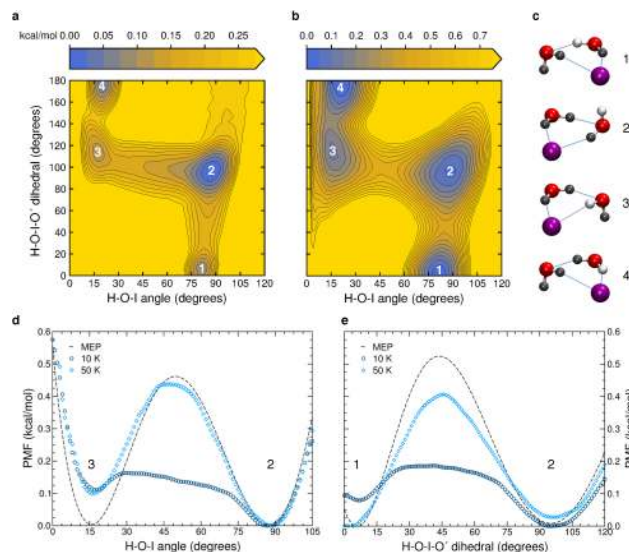


Figure 5: **Probing local free energies of different H-bonding environments in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue of the iodide–dihydrate complex.** **a** and **b**, Two-dimensional quantum potential of mean forces (PMFs) along the iodide–water and water–water H-bond bifurcation pathways (defined by the H-O-I angle on the x -axis and the H-O-I-O' dihedral on the y -axis, respectively) in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue calculated from PIMD well-tempered metadynamics simulations carried out at 10 K (**a**) and 50 K (**b**). Also indicated with 1, 2, 3, and 4 are the H-bond arrangements corresponding to the schematic representations shown in panel **c**. **c**, Schematic representations of the four H-bonding environments experienced by the H atom in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue. The oxygen, hydrogen, and deuterium atoms are shown in red, white, and gray, respectively. **d** and **e**, One-dimensional quantum potential of mean forces (PMFs) along the H-O-I angle and H-O-I-O' dihedral of the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue, respectively, calculated from PIMD well-tempered metadynamics simulations. Also indicated with 1, 2, and 3 are the H-bond arrangements corresponding to the schematic representations shown in panel **c**.

configuration 2 is at least 0.1 kcal/mol lower in free energy than the other configurations, which corresponds to a temperature of ~ 50 K. Consequently, the other configurations will be stable and appreciably populated only at temperatures above 50 K.

Estimates of kinetic rates based on path-integral quantum transition state theory (PI-TST), with a neglect of any dynamical correction accounting for the possibility of barrier recrossing and quantum coherence, indicates that the timescales for both iodide–water and water–water H-bond bifurcations in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ at 10 K are on the order of milliseconds, and between 3 and 4 orders of magnitude slower than in $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ (see Section S3 of the Supplementary Information). It should be noted, however, that PI-TST provides an approximation to a quantum rate, especially in the deep tunneling regime at low temperature where, neglecting coherent dynamical effects, it can only be used to determine an upper bound for the actual quantum rate. In addition, compared to experiment, even small differences in barrier heights, which may be due to inaccuracies in the representation of the underlying Born-Oppenheimer potential energy surface, can result in large variations in the corresponding quantum rates. This implies that, in the present analysis, PI-TST rates can only serve to emphasize qualitative differences in the timescales associated with H-bond rearrangements in $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$, on one side, and $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$, on the other side.

As the temperature increases, both 1D quantum free-energy profiles associated with the iodide–water and water–water H-bond bifurcations approach the corresponding Born-Oppenheimer minimum energy paths, leading to significantly faster H-bond rearrangements. At 50 K, PI-TST

predicts timescales on the order of tens of nanoseconds for both bifurcations in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$, similar to those predicted for $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$. Importantly, compared to 10 K, the two-dimensional free-energy surfaces shown in Figure 5 indicates that both H-bonded positions of the DD water molecule become relatively more stable at 50 K. This implies that local differences in zero-point energies become increasingly less important as the temperature increases, which thus explains the similarity between PI-TST rates predicted for the three different isotopologues at 50 K.

Discussion

By combining accurate many-body representations of iodide–water and water–water interactions with state-of-the-art quantum dynamics simulations, this study provides first evidence for the existence of tunneling pathways in $\text{I}^-(\text{H}_2\text{O})_2$. A detailed analysis of the underlying mechanisms indicates that tunneling leads to fast H-bond rearrangements mediated by the iodide ion. These rearrangements involve large amplitude rotations of the water OH bonds and result in the four hydrogen atoms exchanging their positions on a picosecond timescale even at low temperature. Identical pathways are observed, upon isotopic substitution, in $\text{I}^-(\text{D}_2\text{O})_2$, although the associated H-bond dynamics is significantly slowed down. Further insights into the competition between iodide-water and water-water interactions, and the role played by nuclear quantum effects are gained from the analysis of H-bond rearrangements in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ isotopologue. By breaking the symmetry along the tunneling pathways, the presence of the hydrogen atom allows for precisely probing quantum free-energies associated with the four different bonding topologies within the complex. Due to local differences in zero-point energies and entropic contributions, it

is found that interconversion between the four different isotopomers of $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ is largely suppressed at low temperature, indicating that the mechanisms associated with H-bond rearrangements in the iodide–dihydrate complex can effectively be manipulated by isotopic substitutions. As the temperature increases, nuclear quantum effects become progressively less important, with all different isotopologues exhibiting similar H-bond dynamics above 75 K. It is interesting to note that alternatively to an increase in temperature, the interconversion in $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ could be facilitated by an inert "messenger-tag" molecule like D_2 or Ar (commonly used in predissociation vibrational spectroscopy) which would increase the density of states that are accessible at low temperatures.

Compared to the water trimer, the present results demonstrate that the iodide ion weakens the water-water H-bond, leading to significantly faster tunneling dynamics. Importantly, the flip rotation, which is the fastest motion in the water trimer becomes the slowest in the iodide–dihydrate complex, due to a higher rotational barrier resulting from iodide–water interactions. Although these results clearly indicate that the iodide ion perturbs water–water H-bond rearrangements, the predicted faster dynamics in the iodide–dihydrate complex is apparently at odds with ultrafast vibrational spectroscopy measurements of salt solutions suggesting that the H-bond dynamics within the first hydration shell of iodide is significantly slowed down compared to that of pure water. This difference can be attributed to the presence of a free OH bond in the iodide–dihydrate complex, which effectively triggers the overall H-bond rearrangement within the complex and enable faster water reorientation along both iodide–water and water–water H-bond bifurcation pathways. In turn, the present quantum simulations of the iodide–dihydrate complex provides indirect evidence

for the importance of cooperative effects in water H-bond rearrangements around iodide ions in solution, which, involving water molecules beyond the first hydration shell, thus slows down the overall dynamics, reversing the trend observed in the gas phase.

The present theoretical analysis thus raises the possibility that faster H-bond dynamics in the first hydration shell of iodide ions may be observed in frustrated systems, such as interfaces, where water molecules H-bonded to the ion can be undercoordinated, with at least one dangling OH bond. Furthermore, since the H-bond rearrangement pathways identified in the iodide–dihydrate complex directly depend on the nature of the iodide–water interaction, ion-specific effects on the H-bond dynamics are predicted to also exist in chloride–dihydrate and bromide–dihydrate complexes, which display similar minimum-energy cyclic structures, and possibly in the first hydration shell of both chloride and bromide ions in solution. Ion-dependent hydrogen bond rearrangements through tunneling may thus exist at the surface of salt solutions where, mediating surface-specific ion effects,⁶ they can have direct implications for heterogeneous interfacial chemical processes.³²

Methods

In all calculations the iodide–water interactions are described by the corresponding many-body MB-nrg PEF introduced in Refs.18,24. PIMD simulations³³ are performed to investigate the temperature dependence of the equilibrium between “closed” and “open” configurations of the iodide–dihydrate complex. In these PIMD simulations, each atom is represented by a Feynman’s ring-polymer³⁴ with a variable number of beads depending on the temperature. RPI calculations^{35,36} are performed to identify the tunneling pathways and corresponding tunneling splitting patterns

for the $\text{I}^-(\text{H}_2\text{O})_2$ and $\text{I}^-(\text{D}_2\text{O})_2$ complexes. Quantum free energies for the two H-bond bifurcation pathways in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ complex are calculated from biased PIMD simulations carried out at 10 K and 50 K using the well-tempered metadynamics method^{31,37} as implemented in the PLUMED plugin.³⁸ For these simulations, the H-O-I angle and H-O-I-O' dihedral in the $\text{I}^-(\text{HOD})(\text{D}_2\text{O})$ complex, which are calculated from the centroid of the ring-polymers associated with the relevant atoms in the PIMD simulations, are chosen as the collective variables to map the underlying quantum free energies. Specific details for the PIMD, RPI, and well-tempered metadynamics simulations are reported in Section S1 of the Supplementary Information.

Data availability Any data generated and analysed for this study that are not included in this Article and its Supplementary Information are available from the authors upon request.

Code availability Computer codes used in this study are available from the authors upon request.

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Author contributions P.B. performed all simulations and data analysis, and co-wrote the paper. J.O.R. guided the RPI calculations and co-wrote the paper. F.P. initiated the project, guided the simulation design and data analysis, and co-wrote the paper.

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